TRC

SAMPLING AND ANALYSIS OF PERCHLORATE IN FERTILIZER (Revision 1)

Prepared for

Perchlorate Study Group

Prepared by

TRC

Irvine, California

<u>Participating Laboratories</u>

American Pacific Corporation - Utah
Del Mar Analytical - California
Montgomery Watson Laboratories - California
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Air Force Research Laboratory - Wright Patterson AFB, Ohio
United States EPA - Georgia
United Technologies Corporation - California

June 1999

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Shreveport, Louisiana

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Project No. 98-346

June 1999

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1.0 INTRODUCTION AND BACKGROUND

1. The presence of naturally-occurring perchlorate has been identified in sodium- and potassium-nitrate mined from caliche deposits in Chile (i.e., in Chilean saltpeter). Chilean saltpeter is used as a nitrate fertilizer throughout the world. Schilt (1979) describes observations of perchlorate in Chilean saltpeter as far back as 1896, with concentrations ranging from trace amounts to just under 7 percent. Levels of perchlorate of 1 to 1.5 percent in refined and crude Chilean saltpeter, respectively, measured in 1914 were also described (Schilt, 1979). A study in 1972 attributed poor soybean growth to elevated concentrations of perchlorate in Chilean nitrate fertilizer. The relatively broad range of perchlorate concentrations was attributed to varying degrees of the liquid recycling during the production of the nitrate salts, and the possible nonuniform distribution of naturally-occurring perchlorate in the caliche. Review of available literature and limited testing of selected samples of chemical fertilizer indicate that some chemical fertilizers contain perchlorate.

2. Based on the above-referenced literature, data and the results of the limited fertilizer sampling and analysis of California fertilizers for perchlorate conducted in August of 1998, additional studies to determine if perchlorate is typically present in nitrate type fertilizers was performed. In order to confirm the above results and also to obtain more information on the presence of perchlorate associated with the use of fertilizers, the following activities were completed, and are presented in this report:
   - Confirmatory sampling and analysis of previously tested products.
   - Collection and analysis of fertilizers nationwide.
   - Collection and analysis of fertilizer raw materials.

2.0 SAMPLING AND ANALYSIS

2.1 SAMPLE COLLECTION

1. To confirm the results of the previous perchlorate data indicated above, samples were obtained from different production lots of the previously tested California fertilizers. These samples were purchased from various commercial suppliers and retail sources.

2. To obtain information on the potential presence of perchlorate associated with the use of chemical fertilizers, additional samples were collected from the Kansas City, Missouri and Long Island, New York areas. Samples of the fertilizers shown in Table 1 were collected from various commercial suppliers and retail sources.

3. As part of this study, samples of two raw materials used in chemical fertilizer production were also collected, Caliche (Chilean nitrate) was obtained from the Aconcagua Nitrate Mine in Calama, Chile by TRC. A Langbeinite (a potassium/magnesium sulfate mineral) ore sample (crushed) was provided by IMC Minerals in Albuquerque, New Mexico.

4. The fertilizers and raw material samples were collected under chain-of-custody procedures and forwarded to the primary laboratory for analysis.

5. The primary laboratory prepared extracts of each sample, which were then shipped to six outside laboratories for confirmatory analysis.

2.2 ANALYSIS

2.2.1 ION-CHROMATOGRAPHY

1. The primary laboratory (Del Mar Analytical, Irvine, California) analyzed the fertilizers using the California Department of Health Services Method of Ion-Chromatography for Perchlorates (Attachment 1). Table 1 provides a summary of the Ion-Chromatography perchlorate results.

2. As discussed above, six outside laboratories analyzed the perchlorate extracts, for confirmation purposes. However, these laboratories did not all perform the analyses using the California DHS Method for perchlorates. Table 2 provides a list of the methods used by each laboratory and the differences between the method used and the California DHS method. Table 1 provides a summary of the results of the analyses conducted by the outside laboratories discussed above. As noted in Table 1, the outside laboratories analyzed a 1:10 extract. The results in Table 1 for the outside laboratories were adjusted by a factor of ten to allow comparison with the primary laboratory data. Copies of the laboratory reports are provided in Appendix A.

2.2.2 TRIPHENYLSTIBONIUM TITRATION

1. As part of this study, one set of the fertilizer extracts, and various control samples prepared by TRC were analyzed using the triphenylstibonium titration method after purification of the extracts using ion exchange resin adsorption. The purpose of performing the titration study was to chemically confirm the presence of perchlorate in the extracts. The triphenylstibonium titration method has been shown to be highly specific for perchlorate, and therefore can be

used to confirm the Ion-Chromatography results, which are highly accurate, but may be less specific in detecting perchlorate. Table 1 also includes a summary of the triphenylstibonium titration results.

3.0 DISCUSSION

1. The results of the sampling and analysis of the fertilizers indicates that perchlorate was present at varying levels in approximately 29 out of the 33 samples tested (i.e., 90 percent). The detectable perchlorate levels in these fertilizers ranged from approximately 2 ppm to over 11,000 ppm with most being greater than 500 ppm. The perchlorate concentration averaged roughly one-half of one percent (0.5 percent or 5,000 ppm), as measured in the 29 fertilizers that were positive for perchlorate. These results indicate that perchlorate levels can vary significantly between fertilizer brands and formulation types. Further, the results of the analysis of different production lots of the previously tested fertilizers showed significant variations between the different lots, indicating either variations in production practices or perchlorate levels in the raw materials. Both raw materials tested, Caliche and Langbeinite contained elevated levels of perchlorate; 30,000 ppm and 13,000 ppm (i.e., 1.3 to 1.5 percent), respectively.

2. A comparison of the perchlorate results from the primary laboratory and the outside laboratories shows an excellent correlation. As indicated in Table 1, the standard deviations are very low, indicating a high level of precision. Table 1 also indicates the various duplicate samples and their results. The duplicate samples were found to generally agree within normal laboratory limits (i.e., ±50 percent), with the exception of one duplicate sample PS-17/PS-24 which showed an unexplained significant difference. This difference is most likely due to an error in the extract preparation, since all of the laboratories had similar results for these samples.

3. The results of the triphenylstibonium titration, appear to generally agree with the ion-chromatography results, although the method appears to slightly over estimate the perchlorate levels. Quality Control (QC) samples submitted to the laboratory containing known levels of perchlorate, chlorate, chlorite, ammonium nitrate and thiosulfate showed no interference with the perchlorate analysis. Additional duplicate samples submitted also showed good correlation, within the expected limits.

TABLE 1

FERTILIZER PERCHLORATE LIQUID CHROMATOGRAPHY TESTING PRELIMINARY RESULTS

	MANUFACTURER	BRAND NAME	N-P K[2] RATIO	PRIMARY CONSTITUENT	TRIPHENYL-STIBONIUM TITRATION (mg/kg)[1]	ION-CHROMATOGRAPHY DEL MAR ANALYTICAL RESULTS (mg/kg)	SPLIT SAMPLE ANALYSIS RESULTS (mg/kg)[1]						STATISTICAL EVALUATION		PERCENTAGE OF PERCHLORATE (%)
							LAB 1	LAB 2	LAB 3	LAB 4	USAF	USEPA	MEAN[12]	STANDARD DEVIATION[13]	
Obtained 1/27/99 Kansas City, Missouri															
PS-11	Scott's	Miracle-Gro Lawn Food	36-6-6	Potash derived from Potassium Nitrate	8,600	7,400	8,160	6,260	8,800	8,290	7,068	12,060	8,291	1,866	0.83
PS-13	Shulte	Rose Plus	19-24-24	Potassium Nitrate	<50	13	<6.0	<40	<0.8	9.6	[11]	9,570[14]	9	8	0.0009
PS-10	Acme	Stump Remover	NA	Potassium Nitrate	<50	<0.4	<6.0	<40	<0.4	<3.0	[11]	0	<3.0	8	<.0003
PS-07	Sudbury	Potash	0-0-44	Potassium Chloride	5,440	4,800	4,730	8,830	5,000	4,920	4,369	6,616	5,609	1,592	0.56
PS-05	Peters	All Purpose Plant Food	20-20-20	Potassium Nitrate	7,150	6,300	6,700	4,760	6,200	6,360	6,898	9,720	6,705	1,497	0.67
PS-14	Jobe's	Plant Food Spikes	16-2 6	Potassium Nitrate	10,350	8,100	9,480	8,640	9,000	9,920	6,896	13,330	9,338	2,016	0.93
PS-01	Fertilome	Start-N-Grow Plant Food	18-6-12	Potassium Nitrate	5,900	4,700	4,680	5,150	5,300	4,710	4,872	5,720	5,019	392	0.5
PS-08	Osmocote	Vegetable and Bedding Plant Food	14-14-14	Ammonium Nitrate	1,250	940	1,090	968	970	1,010	803	1,380	1,023	179	0.1
PS-12[6]	Osmocote	Vegetable and Bedding Plant Food	14-14-14	Ammonium Nitrate	750	540	636	597	530	580	526	530	563	43	0.06
PS-02	Ringer	Supreme Gardens	7/7/07	Nitrate of Soda	2,950	3,200	3,490	2,360	3,100	3,240	3,077	4,650	3,302	689	0.33
PS-09[5]	Ringer	Supreme Gardens	7/7/07	Nitrate of Soda	5,200	3,900	4,380	5,120	4,300	4,380	4,049	6,230	4,623	807	0.46
PS-03	Peters	Lawn Food	38-4-4	Potassium Nitrate	9,900	8,600	8,950	7,730	9,400	8,860	7,678	12,670	9,127	1,686	0.91
PS-04	HiYield	Nitrate of Soda	16-0-0	Nitrate of Soda	6,800	7,400	7,620	6,300/11,840[10]	8,000	7,660	6,908	10,340	8,153	1,175	0.81
Obtained 1/28/99 Long Island, New York															
PS-15	Ringer	Lawn Restorer	10/2/06	Nitrate of Soda	6,140	5,300	6,060	5,190	6,100	6,080	4,673	8,840	6,035	1,353	0.6
PS-21[8]	Ringer	Lawn Restorer	10/2/06	Nitrate of Soda	3,400	2,400	2,960	2,560	2,900	3,000	2,376	3,410	2,801	375	0.28
PS-20	Frank's	Grow	15-30-15	Muriate of Potash	6,250	5,400	5,380	10,000	4,800	5,560	7,098	4,240	6,068	1,943	0.6
PS-16	Peters	All Purpose Plant Food	20-20-20	Potassium Nitrate	6,980	7,300	7,510	5,640	7,400	7,210	6,194	12,550	7,686	2,257	0.77
PS-19	Osmocote	Vegetable and Bedding Plant Food	14-14-14	Ammonium Nitrate	3,100	2,500	2,650	3,270	2,700	2,660	2,053	3,840	2,810	578	0.28
PS-18	Osmocote	Outdoor and Indoor Plant Food	18-6-12	Ammonium Nitrate	740	600	733	832/993[10]	750	690	904	160	678	255	0.07
PS-23	Vigoro	Tomato and Vegetable Plant Food	10/8/14	Muriate of Potash, Sul Po Mag	450	360	464	738	340	430	514	970	545	229	0.05
PS-17	Jonathan Green	Fall Fertilizer	10/18/20	Muriate of Potash	<50	<0.4	<6.0	<40	2.2	<3.0	[11]	0	4	8	0.0004
PS-24[7]	Jonathan Green	Fall Fertilizer	10/18/20	Muriate of Potash	2,850	2,400	2,590	2,840	2,200	2,480	2,530	3,970	2,716	586	0.27
PS-22	Scotts	Miracle-Gro Lawn Fertilizer	31-3-9	Muriate of Potash	1,700	1,300	1,549	2,646	1,400	1,530	1,995	1,680	1,729	462	0.17
Obtained from California Source															
PS-31	CNC[3]	Champion Potassium Nitrate	13.5-0-45	--	16,800	12,000 (7,500)[4]	13,290	14,380	13,000	15,100	11,749	21,140	14,058	5,947	1.40
PS-33	Best[3]	K-Power Potassium Nitrate	13.75-0-46	--	8,250	7,100 (27,500)[4]	7,563	2,600	7,400	7,870	7,201	10,140	8,582	4,455	0.85
PS-28	Grow More Corp[2]	Grow More	6/30/30	--	2,800	2,500 (<4,000)[4]	2,599	3,623	2,200	2,490	3,135	7,270	3,509	2,101	0.35
PS-25	Best[3]	Triple Sixteen	16-16-16	--	5,250	4,200 (18,000)[4]	4,223	3,680	4,000	4,310	3,727	7,050	5,441	2,754	0.54
PS-26	Bandini[3]	Sul Po Mag	0-0-22	--	3,550	3,000 (15,000)[4]	3,073	4,810	3,200	3,160	2,834	4,510	4,369	2,180	0.43
PS-27	Plant Marvel	Natriculture	12/31/14	Potassium Nitrate	6,300	5,300	6,680	7,120	5,500	6,450	6,246	17,440	7,819	4,290	0.78
PS-29	Dexol	Stump Remover	Unknown	Unknown	5,800	4,900	5,189	5,290	5,400	5,420	4,576	6,730	5,358	676	0.53
PS-32	K Power	Mini Prills	13.75-0-46	Chileans Nitrate	8,200	6,300	6,381	6,300	6,100	6,560	5,862	8,530	6,576	889	0.65
PS-06	Peters	All Purpose	20-20-20	Potassium Nitrate	3,400	3,190	3,220	3,680	3,000	3,090	3,128	4,740	3,435	615	0.34
Sample of Raw Materials and Control Sample 2/8/99															
PS-34	--	Caliche (Chilean Nitrate Source)	Unknown	Sodium Nitrate	32,800	30,000	26,310	32,980	27,000	30,900	26,120	41,350	30,666	5,371	3.06
PS-30	IMC Group	Langbeinite Ore	Unknown	*Magnesium, Sulfur, Potassium*	15,600	13,000	14,300	20,090	14,000	16,400	13,649	21,160	16,086	3,288	1.6
LCS-1[9]	--	--	Unknown	--	90	--	96	99	100	94	99	--	98	2	0.009
LCS-2[9]	--	--	Unknown	--	105	--	104	94	99	97	98	--	98	4	0.009
Blank	--	--	Unknown	--	<50	--	<0.003	<0.003	<0.004	<0.003	--	0	<0.001	0.0007	0.000001

[1] Laboratory extract results (mg/L) were converted to mg/kg units for comparative purposes, by multiplying the result by 10 to account for the 1:10 dilution used to prepare the extracts

[2] Nitrogen, Phosphorus and Potassium Levels

[3] Repeat of Prior Testing

[4] Prior Testing Results

[5] Duplicate for PS-02

[6] Duplicate for PS-08

[7] Duplicate for PS-17

[8] Duplicate for PS-15

[9] Laboratory Control Standard of 100 ppb Quality Control Samples [9][10]

[10] *Interim duplicate sample analysis*

[11] Due to interferences, no value was reported

[12] Mean values calculated from results obtained by Del Mar Analytical, Labs 1 through 4 as noted, the United States Air Force and the United Environmental Protection Agency. For samples with duplicate analyses, the duplicate results were averaged before calculating the overall mean and standard deviation

[13] Standard deviation values calculated from results obtained by Del Mar Analytical, Labs 1 through 4 as noted, the United States Air Force and United States Environmental Protection Agency. For samples with duplicate analyses, the duplicate results were averaged before calculating the overall mean and standard deviation

[14] Considered an outlier - not used for statistical evaluation

TABLE 2

SUMMARY OF ION-CHROMATOGRAPHY METHODS

LABORATORIES	SIGNIFICANT DIFFERENCES BETWEEN OUTSIDE LABORATORY PROCEDURES AND DHS PERCHLORATE METHOD
Del Mar Analytical	• Used 4 mm Standard Bore Column (AS-11)
American Pacific	• Used 4 mm Standard Bore Column (AS-16)
UTC	• Used 4 mm Standard Bore Column (AS-11) • Used 100 mM NAOH Without Ion-Suppressor
Montgomery Watson	• Used 4 mm Standard Bore Column (AS-11)
Thiokol Propulsion Group	• Used 4 mm Standard Bore Column (AS-11) • Used 100 mM NAOH With Ion-Suppressor AS-RS-ULTRA
U.S. Air Force	• Used 2 mm Micro Standard Bore Column (AS-11)
U.S. EPA	• Used 4 mm Standard Bore Column (AS-11)

98-346/Sa&AnPeFe (Rev. 1) (6/18/99/rm)